Supplementary Information for: Weiss, B. P., S. S. Kim, J. L. Kirschvink, R. E. Kopp, M. Sankaran, A. Kobayashi, and A. Komeili (2003) Ferromagnetic resonance and low temperature magnetic tests for biogenic magnetite, *Earth Planet. Sci. Lett.*, submitted

A. Introduction

Here we briefly review the ways in which FMR spectra can be used to infer the crystal and compositional properties of natural samples. Since all of our samples are composed of many tiny, randomly oriented crystallites, we restrict the rest of the discussion on FMR spectra to the polycrystalline case. The FMR spectrum of such polycrystalline samples is known as a "powder pattern". There is a well developed theory for rapidly obtaining magnetic and compositional parameters from such powder patterns using simple analytic expressions. Except where noted, the following discussion focuses on FMR measurements at room temperature only. Also except where noted, the discussion assumes that the crystallites are non-interacting, SD, and sufficiently small in size such that eddy current effects can be neglected. Eddy current effects in FMR spectra, which only become important for magnetite crystal diameters >~5 μm [1], should be unimportant for our samples. However, some of our samples, particularly the extracellular magnetites and synthetic magnetites, do have strong self-interactions.

B. FMR Parameters

As described in the main manuscript, we classified the FMR spectra of each of our FMR spectra using three of the following parameters: the polycrystalline effective *g*-factor, g_{eff}, the linewidth (ΔB and ΔB_{FWHM}), and the asymmetry ratio, A (see Fig. 2a). The true g-factor is defined $g \equiv h\upsilon/\beta B_{rfe}$ where h is Planck's constant, υ is the X-band microwave frequency (9.3 GHz), β is the Bohr magneton, and B_{rfe} is the applied field at which maximum absorption occurs assuming the sample has no magnetic anisotropy (for magnetite $g = 2.12$ [2]). Samples with anisotropy fields will have a peak absorption at a field B_{eff} different from B_{rfe}, which we use to define an effective g-factor, $g_{eff} \equiv h\upsilon/\beta B_{eff}$. Therefore, g_{eff} is specified by both the zero-crossing in the derivative spectrum and the peak absorption in the integrated spectrum (Fig. 2a). The effective g-factor was first defined by Okamura [3], but is not widely used in the modern literature because simple

relations between g_{eff} and the anisotropy constants are only known for a small a few types of anisotropy fields (for instance, cubic magnetocrystalline [4]). We report g_{eff} because the relationship between g_{eff} and g gives valuable information about the identify of the sample's anisotropy and crystal size.

The linewidth is a characteristic measure of the spread in field values over which resonance is observed to occur. It can be defined in several ways, including the distance between the maximum positive and negative peaks in the derivative spectrum (ΔB), or as the full-width at half maximum of the integrated (e.g., true absorption) spectrum (ΔB_{FWHM}) (Fig. 2a). In this paper, except where otherwise noted we use the former definition, although we report both values (Table 2). Following early workers in FMR [4, 5], we define the asymmetry ratio as $A \equiv \Delta B_{high}/\Delta B_{low}$, where ΔB_{high} is the linewidth on the high-field side of the absorption peak (which is at B_{eff}) and ΔB_{low} is the linewidth on the low-field side of B_{eff} (Fig. 2a). Both ΔB_{high} and ΔB_{low} are half-linewidths at half maximum in the integrated spectrum, such that $\Delta B_{FWHM} = \Delta B_{high} + \Delta B_{low}$, but are not usually equal since most spectra have an asymmetric shape.

It is important to remember that these four parameters do not always have a simple physical meaning. They are used here only to summarize the defining characteristics of a large number of spectra such that general features of each spectrum can be quickly compared. For detailed interpretation of the FMR properties of individual samples, there is no substitute for direct examination of the FMR spectrum. The sizes of $g_{eff,}$ ΔB, and A give information about the strength and orientation of a sample's anisotropy fields, crystal size and composition.

C. Dependence of FMR on magnetic anisotropy

1. Overview. For equant crystals with cubic structure like magnetite and other ferrites, the peak-to-peak linewidth is (assuming only first order contributions to the anisotropy) [4, 6, 7]:

$$\Delta B_a \sim 5/3 H_K = 5/3\ (2K_1/M_s) \qquad (1)$$

for the microscopic coercivity, H_K, the first order cubic magnetocrystalline anisotropy constant, K_1, and saturation magnetization, M_s. Cubic ferromagnets with negative (positive) K_1, have a {111} ({100}) magnetocrystalline easy axis and a {100} ({111})

hard axis. For cubic samples, the resonance field of the free electron in the absence of anisotropy fields, B_{rfe}, is given by $B_{rfe} \sim B_{max}$ - $3/5\Delta B_a$ (when $K_1 < 0$) and $B_{rfe} \sim B_{max}$ - $2/5\Delta B_a$ (when $K_1 > 0$), where B_{max} is the high-field absorption peak [1]. The latter two relations allow one to obtain the true g-factor using $g = h\upsilon/\beta B_{rfe}$. They imply that cubic samples with negative (positive) K_1 will have $A > 1$ ($A < 1$) (for a graphical visualization of this, see [4-7]). Computer modeling also shows that cubic samples with negative (positive) K_1 will have g_{eff} greater (less) than the mineral's g-factor [6, 7].

Following Griscom [1] and using equation (5.35) of ref. [8], the peak-to-peak linewidth of samples dominated by uniaxial anisotropy (which can result from shape, crystal structure, or magnetoelasticity), is given by:

$$\Delta B_u \sim 3/2H_K$$

$$= 3/2\mu_0(N_b - N_a)M_s \text{ (shape anisotropy)} \quad (2)$$

$$= 3/2(2K_u/M_s) \text{ (magnetocrystalline anisotropy)} \quad (3)$$

$$= 3/2(3\lambda_s\sigma/M_s) \text{ (magnetoelastic anisotropy)} \quad (4)$$

where K_u is the uniaxial magnetocrystalline anisotropy constant, N_b and N_a are the demagnetizing factors perpendicular and parallel to the shape axis of rotational symmetry, λ_s is the isotropic magnetostriction, σ is the stress, and μ_0 is the permeability of free space. Crystals with $\Delta B_u > 0$ are said to have positive uniaxial anisotropy, while samples with $\Delta B_u < 0$ are said to have negative uniaxial anisotropy. Examples of positive uniaxial anisotropy of the former are prolate spheroids, which have $N_b > N_a$, minerals like goethite, which have uniaxial magnetocrystalline anisotropy with $K_u > 0$, and minerals like hematite, which are dominated by magnetostriction for which $\lambda_s > 0$. Examples of negative uniaxial anisotropy are oblate spheroids, which have $N_b < N_a$. It is easy to show, following similar calculations for cubic anisotropy [7, 9], that $B_{rfe} \sim B_{max}$ - $1/3\Delta B_a$ (for positive uniaxial anisotropy) and $B_{rfe} \sim B_{max}$ - $2/3\Delta B_a$ (negative uniaxial anisotropy) which again permits estimation of the true g-factors. These relations imply that uniaxial samples with positive (negative) uniaxial anisotropy have $A < 1$ ($A > 1$) (for a graphical visualization of this, see [1, 10-12]).

The minimum linewidth of magnetite and maghemite crystals will be obtained for non-interacting equant grains that only have magnetocrystalline anisotropy. In this case, using equation (1) and M_s and K_1 from [8], magnetite will have $\Delta B \sim \Delta B_a \sim 94$ mT and

maghemite will have $\Delta B_a \sim 40$ mT. Each of these equations will underestimates the true linewidths for crystal assemblages that are magnetostatically interacting and/or have multiple forms of anisotropy. We also note that the above equations are only strictly true for very weak anisotropy: samples with large enough absolute anisotropy (regardless of its sign and angular dependence) will show enhanced secondary absorption peaks on the low-field side of the mineral's *g*-factor because the anisotropy will divert the crystal moments away from the applied field [1, 6, 10-14].

2. FMR theory and modeling for uniaxial anisotropy. Surig *et al*. [13, 14] directly computed the FMR spectra of polycrystalline materials with positive and negative uniaxial anisotropy for a wide range of saturation magnetization values. Their results show how the FMR spectra of minerals with positive (negative) uniaxial anisotropy have $A > 1$ ($A < 1$) (see above). Elongate magnetite crystals, which have M_s = 480 kA m^{-1} would have an FMR spectrum intermediate between curves B and C of Fig. 3 of [14]. This shows how magnetites with prolate shapes (oblate shapes) should have g_{eff} slightly less than 2.12 (greater than 2.12), $A < 1$ ($A > 1$) and might also have a low-field absorption peak in the derivative spectrum. Elongate magnetites should also have ΔB up to three times that of magnetite with only magnetocrystalline anisotropy.

The extended low-field (high-field) absorption property of materials with positive (negative) uniaxial anisotropy can also be directly observed from the resonance condition [15]

$$B_{0,a} = (N_a - N_b)\mu_0 M_s + B_{rfe}$$
$$B_{0,b} = \left[N_b - \frac{1}{2}(N_a + N_b)\right]\mu_0 M_s + \sqrt{\frac{1}{4}(N_a - N_b)^2(\mu_0 M_s)^2 + {B_{rfe}}^2} \qquad (5)$$

where $B_{0,a}$ and $B_{0,b}$ are, respectively, the resonance field for a single uniaxial crystal with the applied field parallel and perpendicular to the axis of symmetry (e.g., axis elongation or flattening). For the powder pattern of elongate magnetite ellipsoids with axial ratios of 0.1, using the ellipsoidal demagnetizing factors as given by [16] we find from equation (5) that $B_{0,a}$ = 19 mT and $B_{0,b}$= 490 mT. This predicts that $\Delta B \sim B_{0,b} - B_{0,a}$ = 470 mT and $A \sim (B_{0,b} - B_{rfe})/(B_{rfe} - B_{0,a}) = 0.6$, in good agreement with equation (2) which gives $\Delta B \sim$

420 mT. This demonstrates why direct numerical modeling [13, 14] gives $A < 1$ for these types of positive uniaxial materials.

D. Dependence of FMR on crystal size

FMR spectra also give information on the size of the ferromagnetic crystals. Compared to single domain assemblages of the same mineralogy, superparamagnetic crystals of will have narrower linewidths (small ΔB), nearly symmetric absorption ($A \sim 1$), and g_{eff} closer to the mineral's g-factor [17, 18]. Superparamagnetic assemblages of magnetites will show broader, more asymmetric linewidths (e.g, larger ΔB and A farther from 1) and higher g_{eff} at 77 K compared to room temperature (e.g., [19, 20]). However, because FMR absorption and linewidth are smooth functions of particle size with no discontinuities across the single domain superparamagnetic boundary, there is no concept of "blocking temperature" in FMR [9]. Multidomain assemblages will typically have large ΔB [7] with very large g_{eff} (typically well above the free electron value of 2), $A > 1$, and a high-field absorption peak near the field value at which saturation occurs (for equidimensional crystals, this would be at $\sim 1/3\mu_0 M_s$, which is 200 mT and 160 mT for magnetite and maghemite, respectively) [9, 21]. The large g_{eff} and $A > 1$ of these coarse grained samples is a natural geometric consequence of their large ΔB: because the first derivative of the absorption with respect to field is an odd function of the field (see [22]), samples with large linewidths have enhanced low-field absorption due to absorption by crystals magnetized in directions different from that of the applied field.

E. Dependence of FMR on composition

Measurements of the sign and magnitude and angular dependence of the anisotropy (see Section A) can be used as compositional indicator. This can be enhanced by FMR measurements at low temperatures, which can identify remanence transitions and behavior characteristic of mineralogy and stoichiometry as in standard low-temperature magnetometry [7, 23].

Paramagnetic ions can be rapidly distinguished from ferromagnets by their characteristic fine and hyperfine structure and characteristic g-factors [24-26]. Their g-factors are usually temperature-independent while their absorption intensity is inversely

proportional to temperature [7, 23, 27]. For ferromagnetic minerals, g_{eff}, ΔB, and the line intensity each have a wide variety of dependencies on temperature by which these minerals can often be distinguished [9, 17, 23, 28]. For instance, magnetite has a characteristic discontinuous change in its FMR spectrum when cooled or warmed across its ~125 K Verwey transition.

References

[1] D.L. Griscom, Ferromagnetic resonance spectra of lunar fines: some implications of line shape analysis, Geochim. Cosmochim. Acta 38 (1974) 1509-1519.

[2] L.R. Bickford, Ferromagnetic resonance absorption in single magnetite crystals, Phys. Rev. 78 (1950) 449-457.

[3] T. Okamura, Y. Torizuka and Y. Kojima, The g factor of ferrites, Phys. Rev. 88 (1952) 1425-1426.

[4] P.J.B. Clarricoats, Microwave Ferrites, John Wiley and Sons Inc., New York, 1961.

[5] J.E. Pippin and C.L. Hogan, Resonance measurements on nickel-cobalt ferrites as a function of temperature and nickel ferrite-aluminates, IRE Trans. MTT 6 (1958) 77-82.

[6] E. Schlomann and J.R. Zeender, Ferromagnetic resonance in polycrystalline nickel ferrite aluminate, J. Appl. Phys. 29 (1958) 341-343.

[7] D.L. Griscom, Ferromagnetic resonance of precipitated phases in natural glasses, J. Non-Cryst. Solids 67 (1984) 81-118.

[8] D.J. Dunlop and O. Ozdemir, Rock Magnetism: Fundamentals and Frontiers, 573 pp., Cambridge University Press, New York, 1997.

[9] D.L. Griscom, Ferromagnetic resonance of fine grained precipitates in glass: A thumbnail review, J. Non-Cryst. Solids 42 (1980) 287-296.

[10] E. Schlomann and R.V. Jones, Ferromagnetic resonance in polycrystalline ferrites with hexagonal crystal structure, J. Appl. Phys. 30 (1959) 177S- 178S.

[11] C.A. Morrison and N. Karayianis, Ferromagnetic resonance in uniaxial polycrystalline materials, J. Appl. Phys. 29 (1958) 339-340.

[12] D.L. Griscom, E.J. Friebele and C.L. Marquardt, Evidence for a ubiquitous, sub-microscopic "magnetite-like" constituent in the lunar soils, Proc. Fourth Lunar Sci. Conf. 3 (1973) 2709-2727.

[13] C. Surig, K.A. Hempel and F. Schumacher, Microwave absorption in single-domain particles involving first- and second-order uniaxial magnetic anisotropy constant, J. Magn. Magn. Mat. 117 (1992) 441-447.

[14] C. Surig, K.A. Hempel, R.A. Muller and P. Gornert, Investigations on $Zn_{2-x}Co_xW$-type hexaferrites powders at low temperatures by ferromagnetic resonance, J. Magn. Magn. Mat. 150 (1995) 270-276.

[15] D.L. Griscom, C.L. Marquardt, E.J. Friebele and D.J. Dunlop, Magnetic hysteresis in the F.M.R. spectra of fine-grained spherical iron: Possible evidence

for a new carrier of hard remanence in lunar rocks and soils, Earth Planet. Sci. Lett. 24 (1974) 78-85.
[16] R.I. Joseph, Demagnetizing factors in nonellipsoidal samples--a review, Geophysics 41 (1976) 1052-1054.
[17] R.S. deBiasi and T.C. Devezas, Anisotropy field of small magnetic particles as measured by resonance, J. Appl. Phys. 49 (1978) 2466-2469.
[18] V.M. Malhotra and W.R.M. Graham, Detection of magnetite particles in coal by ferromagnetic resonance, J. Appl. Phys. 57 (1985) 1270-1276.
[19] K. Abe, Y. Miyamoto and S. Chikazumi, Magnetocrystalline anisotropy of low temperature phase of magnetite, J. Phys. Soc. Japan 41 (1976) 1894-1902.
[20] A.R. Muxworthy and E. McClelland, Review of the low-temperature magnetic properties of magnetite from a rock magnetic perspective, Geophys. J. Int. 140 (2000) 101-114.
[21] R.F. Soohoo, Theory and Application of Ferrites, Prentice-Hall, Englewood Cliffs, 1960.
[22] D.L. Griscom, C.I. Merzbacher, N.E. Bibler, H. Imagawa, S. Uchiyama, A. Namiki, G.K. Marasinghe, M. Mesko and M. Karabulut, On the structure and radiation chemistry of iron phosphate glasses: New insights from electron spin resonance, Mossbauer, and evolved-gas spectroscopy, Nucl. Instr. and Meth. in Phys. Res. B 141 (1998) 600-615.
[23] D.L. Griscom, V. Beltran-Lopez, C.I. Merzbacher and E. Bolden, Electron spin resonance of 65-million-year-old glasses and rocks from the Cretaceous-Tertiary boundary, J. Non-Cryst. Solids 253 (1999) 1-22.
[24] A.B. Vassilikou-Dova and G. Lehmann, Investigations of minerals by electron paramagnetic resonance, Fortschr. Miner. 65 (1987) 173-202.
[25] G. Calas, Electron paramagnetic resonance, in: Spectroscopic Methods in Mineralogy and Geology, F.C. Hawthorne, ed., Reviews in Mineralogy Vol. 18, Mineralogical Association of America, Chelsea, 1988.
[26] A. Pawse, S. Beske-Diehl and S.A. Marshall, Use of magnetic hysteresis properties and electron spin resonance spectroscopy for the identification of volcanic ash: a preliminary study, Geophys. J. Int. 132 (1998) 712-720.
[27] D.L. Griscom, C.L. Marquardt and E.J. Friebele, Microwave resonance thermomagnetic analysis: A new method for characterizing fine-grained ferromagnetic constituents in lunar materials, J. Geophys. Res. 80 (1975) 2935-2946.
[28] R.S. deBiasi and W.S.D. Folly, Use of ferromagnetic resonance to determine the size distribution of magnetic particles, Physica B 321 (2002) 117-119.